Vapor-Liquid Equilibria at High Pressures: Calculation of Partial Molar Volumes in Nonpolar Liquid Mixtures

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Thermodynamic analysis of high-pressure vapor-liquid equilibria requires information on the effect of pressure on liquid phase fugacities; this information is given by partial molar volumes in the liquid mixture. A method for predicting these partial molar volumes is presented here. First, molar volumes of saturated liquid mixtures are computed by extending to mixtures the corresponding states correlation of Lyckman and Eckert. These mixture volumes are then used to calculate partial molar volumes with an expression based on a modification of the Redlich-Kwong equation. At high pressures partial molar volumes are strong functions of the composition and in the critical region, may be positive or negative. Calculations are sensitive to the characteristic energy between dissimilar molecules; this energy is generally lower than that given by the geometric-mean rule. Calculated results are in good agreement with experimental data for seven systems containing paraffinic and aromatic hydrocarbons, carbon dioxide, and hydrogen sulfide.

To be useful, a thermodynamic treatment of high-pressure vapor-liquid equilibria must describe how the fugacity of each component, in each phase, depends on the temperature, pressure, and composition. In the vapor phase, this dependence is given by the fugacity coefficient which can be found from vapor-phase volumetric properties as given by an equation of state. In the liquid phase it is more convenient to express the fugacity of a component as the product of the mole fraction, an arbitrary standard state fugacity and an activity coefficient; the effect of temperature, pressure, and composition on the fugacity of a component in the liquid phase is determined by the effect of these variables on the activity coefficient. In this work we are concerned with the effect of pressure on the activity coefficient.

At low or moderate pressures, liquid-phase activity coefficients are very weakly dependent on pressure and, as a result, it has been customary to assume that, for practical purposes, activity coefficients depend only on temperature and composition. In many cases this is a good assumption but for phase equilibria at high pressures, especially for those near critical conditions, it can lead to serious error.

When the standard state fugacity is defined at a constant pressure, then for any component i the pressure dependence of the activity coefficient γ_i is given exactly by

$$\left(\frac{\partial \ln \gamma_i}{\partial P}\right)_{T,x} = \frac{\bar{v}_i}{RT} \tag{1}$$

On the other hand, when the standard state fugacity is defined at the total pressure of the system, Equation (1) must be modified to

$$\left(\frac{\partial \ln \gamma_i}{\partial P}\right)_{T,x} = \frac{\bar{v}_i - v_i^0}{RT} \tag{1a}$$

By judicious choice, it is sometimes possible to use a standard state such that $\bar{v}_i \approx v_i^0$, in which case the activity coefficient is very nearly independent of pressure (*17*). However, since $\bar{v}_i$ is a function of composition, whereas v_i^0 is not, such a happy choice of standard state can make the right-hand side of Equation (2) very small over only a narrow range of composition. At high pressures in the critical region, $\bar{v}_i$ is usually a strong function of composition, especially for heavy components where $\bar{v}_i$ frequently changes sign as well as magnitude.

Experimental activity coefficients obtained at P, the total pressure of the system, can be corrected to a constant, arbitrary reference pressure P^r by integration of Equation (1):

$$\gamma_i^{(P^r)} = \gamma_i^{(P)} \exp \int_P^{P^r} \frac{\bar{v}_i}{RT} dP \tag{2}$$

Equation (2) defines adjusted, pressure-independent activity coefficients $\gamma_i^{(P^r)}$, which at constant temperature, satisfy the isobaric, isothermal Gibbs-Duhem equation. It is advantageous to use such adjusted activity coefficients since their composition dependence can be expressed by simple algebraic functions such as those of Margules, van Laar, etc. Through Equation (2) the effect of pressure is separated from the effect of composition and, as a result, interpretation and correlation of phase equilibrium data are very much facilitated (*18*).

Experimental data for partial molar volumes are rare for binary systems and for multicomponent systems there are essentially none. Since thermodynamic analysis or prediction of multicomponent high-pressure phase equilibria requires partial molar volumes, we require a reliable method for calculating partial molar volumes from a minimum of experimental information. In the following, we present such a method, applicable up to critical compositions, for calculating partial molar volumes in multicomponent liquid mixtures at saturation.

PARTIAL MOLAR VOLUME FROM AN EQUATION OF STATE

The partial molar volume of component k in a mixture of N component is defined by

$$\bar{v}_k = \left(\frac{\partial V}{\partial n_k}\right)_{P,T,n_i(i \neq k)} \tag{3}$$

The partial molar volume can be evaluated from a suitable equation of state for the liquid mixture. Since most equations of state are explicit in pressure, rather than in volume, it is convenient to rewrite Equation (3):

$$\bar{v}_k = \frac{-\left(\dfrac{\partial P}{\partial n_k}\right)_{T,V,n_i(i \neq k)}}{\left(\dfrac{\partial P}{\partial V}\right)_{T,n_i(\text{all } i)}} = f(x, T, v) \tag{4}$$

With an equation of state, Equation (4) gives $\bar{v}_k$ as a function of the composition, temperature, and molar volume of the liquid mixture. Pressure does not appear explicitly in Equation (4), but is implicit in the volume which depends on the pressure.

For practical applications in vapor-liquid equilibria, we require partial molar volumes at saturation; therefore, we need the saturated molar volume of the liquid mixture in Equation (4). Before discussing Equation (4) in more detail, we describe a method for calculating the molar volume of a saturated liquid mixture.

SATURATED MOLAR VOLUME OF LIQUID MIXTURES UP TO A REDUCED TEMPERATURE OF 0.93

Given only the temperature and composition, it is possible, in principle, to calculate the saturated volume of a liquid mixture from an equation of state. Such a calculation, however, requires an equation of state capable of describing accurately both vapor and liquid phases of multicomponent systems. For a wide variety of mixtures, no such equation of state is known. (In fact, the entire problem of phase equilibria at any pressure could be completely solved if such an equation of state were available.) A more realistic and fruitful approach is provided by a corresponding-states correlation specifically developed for saturated liquids. Such a correlation was given by Lyckman and Eckert (*11*), who slightly revised Pitzer's tables (*15*) for the saturated liquid volume of pure substances. In this correlation, the reduced saturated volume is given by

$$v_R = v_R^{(0)} + \omega v_R^{(1)} + \omega^2 v_R^{(2)} \tag{5}$$

where ω is the acentric factor (*15*, *19*) and $v_R^{(0)}$, $v_R^{(1)}$, and $v_R^{(2)}$ are functions of reduced temperature which have been tabulated for reduced temperatures from 0.560 to 0.990 (*11*). To facilitate calculations with an electronic computer, we fitted the tabulated values with the following relation:

$$v_R^{(j)} = a^{(j)} + b^{(j)} T_R + c^{(j)} T_R^2 + d^{(j)} T_R^3 + e^{(j)}/T_R + f^{(j)} \ln (1 - T_R) \tag{6}$$

where $a^{(j)}$ to $f^{(j)}$ are coefficients for $v_R^{(0)}$, $v_R^{(1)}$ and $v_R^{(2)}$; these coefficients are given in Table 1.

TABLE 1. COEFFICIENTS IN EQUATION (6) FOR REDUCED VOLUMES OF SATURATED LIQUIDS†

j	$a^{(j)}$	$b^{(j)}$	$c^{(j)}$	$d^{(j)}$	$e^{(j)}$	$f^{(j)}$
0	0.11917	0.009513	0.21091	−0.06922	0.07480	−0.084476
1	0.98465	−1.60378	1.82484	−0.61432	−0.34546	0.087037
2	−0.55314	−0.15793	−1.01601	0.34095	0.46795	−0.239938

†For reduced temperatures from 0.560 to 0.995.

The reducing parameters for the reduced volume and the reduced temperature are the critical volume and the critical temperature, respectively. For $v_R^{(0)}$, Equation (6) agrees with the originally tabulated values to the fourth significant figure; for $v_R^{(1)}$ and $v_R^{(2)}$ it agrees within ±1 in the fourth significant figure. For pure components, Equations (5) and (6) may be used for reduced temperatures from 0.560 to 0.995. For reduced temperatures above 0.995, the reduced volume may be obtained by first calculating the reduced volumes at T_R of 0.990 and 0.995, and then interpolating to $T_R = 1.0$; by definition $v_R = 1.0$ at $T_R = 1.0$.

Equations (5) and (6) were obtained from pure component data. For application to mixtures, mixing rules for the pseudocritical volume and temperature are necessary. For pseudoreduced temperatures up to 0.93 we suggest the following rules:

$$v_{cM} = \sum_i x_i v_{c_i} \tag{7}$$

$$T_{cM} = \sum_i \sum_j \Phi_i \Phi_j T_{c_{ij}} \tag{8}$$

$$\omega_M = \sum_i \Phi_i \omega_i \tag{9}$$

where

$$\Phi_k = \frac{x_k v_{c_k}}{\sum_i x_i v_{c_i}} \tag{10}$$

$$T_{c_{ij}} = \sqrt{T_{c_{ii}} T_{c_{jj}}}\ (1 - k_{ij}) \tag{11}$$

Because of the small separation between molecules, molecular size is a more important factor in the liquid phase than in the vapor phase. Therefore, in Equations (8) and (9), we use volume fractions rather than mole fractions (or combinations of mole fractions and volume fractions) which were used in previous pseudocritical rules (*6*, *8*, *10*, *20*, *26*).

The constant k_{ij} has an absolute value much less than unity; it represents the deviation from the geometric-mean rule for the characteristic temperature of the i-j pair. To a good approximation, k_{ij} is a constant independent of temperature and density. The binary constant k_{ij} must be evaluated from some binary data (for example, second virial coefficients or solubility), which give information on the nature of i-j interactions. Table 2 gives some of the k_{ij} values used in this work. These values, although obtained from liquid phase measurements, are in good agreement with those obtained by Gunn (*20*) from second virial cross coefficients, and with those reported by Pitzer and Hultgren (*16*) from compressibility factors near the critical region. For paraffin-paraffin systems, experimentally de-

TABLE 2. COMPARISON OF CALCULATED AND EXPERIMENTAL SATURATED MOLAR LIQUID VOLUMES OF BINARY MIXTURES AT HIGH PRESSURES

(Reduced temperature <0.93)

System* (1) (2)	k_{12}	T, °F.	Pressure range, lb./sq. in. abs.	x_2 ($T_R \approx 0.93$)	% Deviation Avg.	% Deviation Max.
n-Butane–carbon dioxide	0.20	100	51.5 to 800	0.68	0.7	1.0
		160	120.6 to 900	0.45	0.2	0.5
		220	241.2 to 600	0.17	0.2	0.5
Propane–methane	0.20	40	79 to 1,200	0.52	0.6	1.6
		100	189 to 950	0.29	0.7	1.2
n-Butane–methane	0.04	100	51.5 to 1,700	0.55	0.7	1.6
		130	80.6 to 1,600	0.47	1.2	2.4
		160	120.6 to 1,400	0.38	1.2	2.1
		190	174.4 to 1,100	0.27	1.2	2.1
		220	241.2 to 800	0.16	0.8	1.1
n-Pentane–methane	0.06	100	15.7 to 2,300	0.68	0.1	0.3
		160	42.5 to 2,100	0.57	0.7	1.9
		220	94.9 to 1,600	0.41	1.2	2.3
		280	185.6 to 900	0.20	1.2	1.8
Propylene–ethane†	0.02	10	58 to 255	—	0.5	0.9
		40	96.4 to 385	—	0.4	0.8
		100	227.3 to 470	0.50	0.5	0.8
Benzene–propane‡	0.03	100	3.2 to 189	—	0.5	1.2
		160	11.1 to 384	1.0	0.8	1.1
		220	29.2 to 520	0.81	0.4	0.7
		280	64.7 to 630	0.64	0.4	1.3
		340	126.0 to 710	0.44	0.5	1.2
		400	222.1 to 630	0.26	0.5	0.9
Hydrogen sulfide–methane	0.04	40	169 to 1,770	0.36	1.0	2.3
		100	394 to 1,500	0.18	1.3	1.7

*Critical constants for pure components taken from the compilation of Kobe and Lynn (9) unless otherwise noted. Experimental data of binary systems are taken from Sage et al. (*24*, *25*).

†Critical volume of ethane is 2.27 cu. ft./lb.-mole as reported by Din (*5*).

‡Critical volume of benzene is 4.06 cu. ft./lb.-mole as reported by Bender et al. (*1*).

termined k_{ij}'s are in good agreement with the semitheoretical relation

$$k_{ij} = 1 - \left[\frac{\sqrt{v_{c_i}^{1/3} v_{c_j}^{1/3}}}{(v_{c_i}^{1/3} + v_{c_j}^{1/3})/2} \right]^n \tag{12}$$

Equation (12) follows from London's theory of dispersion forces, neglecting small differences in ionization potentials. In agreement with Reid and Leland (*23*), we found that $n = 3$ gives better results than the theoretical value $n = 6$. Equation (12), however, is useful only for mixtures of paraffins; for other systems it may lead to large errors.

The saturated liquid volume of a multicomponent mixture may be calculated with Equations (5) and (6) and Equations (7) through (11). The pseudocritical rules, Equations (7) and (8), were found to give good predictions for $T_R \leq 0.93$. For larger T_R (critical region) a modification of the pseudocritical rules is required, as indicated later.

Figures 1 and 2 show calculated saturated liquid volumes for two systems, n-butane–carbon dioxide and propane–methane, each at three different temperatures; the calculated results are compared with experimental data of Sage and Lacey (*21*, *24*, *25*). These figures include the calculations in the critical region to be discussed later. The agreements are quantitative over the relatively wide temperature range.

At 160°F. n-butane is subcritical. As the mole fraction of carbon dioxide rises, the molar volume of the liquid mixture decreases at first, primarily because of the introduction of the smaller molecules of carbon dioxide and partly because of the increase in pressure; meanwhile, the reduced temperature increases due to the lower critical temperature of carbon dioxide. At an intermediate composition, the effect of increasing reduced temperature dominates the effect of smaller molecular size and higher pressure, and the molar volume of the mixture increases sharply toward its critical value. At high concentrations, the supercritical carbon dioxide expands or dilates the subcritical n-butane. This dilative effect becomes particularly pronounced in the critical region; it has been discussed previously in our development of a modified van Laar equation suitable for high-pressure vapor-liquid equilibria (*3*).

At a lower temperature, say 100°F., carbon dioxide is only slightly supercritical, whereas n-butane is well below its critical temperature. At 100°F. the effect of dilation therefore does not become important until very near the critical composition. On the other hand, at a higher temperature (220°F.) the heavier component, n-butane, is already close to its critical temperature and therefore is much more sensitive to the dilative effect of the supercritical carbon dioxide. At 220°F. the molar volume of the mixture increases soon after the introduction of carbon dioxide. Similar behavior is observed in the propane-methane system.

The characteristic parameter k_{ij} is very important in these calculations. To illustrate, Figure 3 shows the saturated liquid volumes for n-butane–carbon dioxide mixtures, calculated with and without correction to the geometric-mean for $T_{c_{12}}$. For this system, the geometric-mean assumption is a poor one as was noted previously by Joffe and Zudkevitch (*7*).

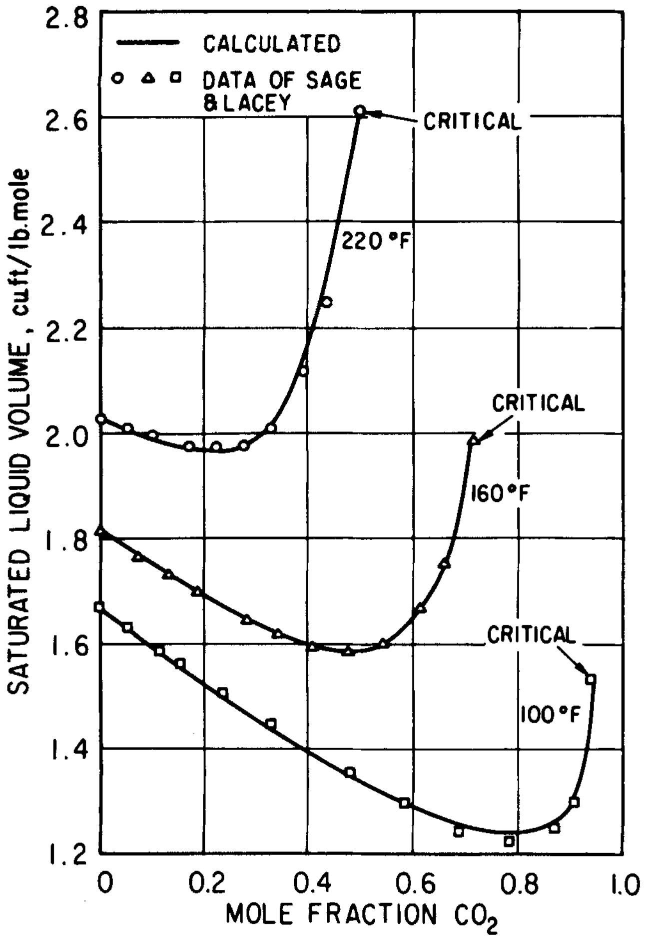

Fig. 1. Saturated liquid molar volumes of *n*-butane–carbon dioxide mixtures.

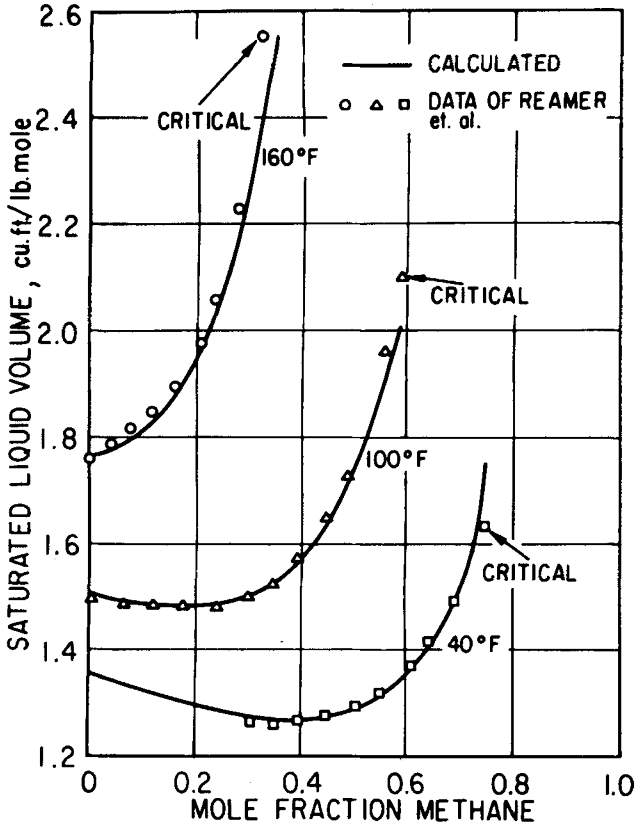

Fig. 2. Saturated liquid molar volumes of propane-methane mixtures.

Table 2 summarizes the results of calculations for seven binary systems, including those containing carbon dioxide, hydrogen sulfide, and aromatic hydrocarbons. The average deviation and maximum deviation for all twenty-five isotherms are small, and are probably of the same order of magnitude as the uncertainty in the experimental data. The rather good agreement for the system *n*-pentane-methane (where the ratio of pure component critical volumes is a little more than three) seems to indicate that the difference in molecular sizes can be adequately taken into account by using volume fractions (rather than mole fractions) in the mixing rules, Equations (8) to (10).

With a reliable method for calculating the volumes of saturated liquid mixtures, we proceed now to calculate partial molar volumes with Equation (4) which requires an equation of state for liquid mixtures.

EQUATION OF STATE FOR LIQUID MIXTURES

For nonpolar liquids, an equation of the van der Waals type provides a reasonable description of volumetric properties. Since the Redlich and Kwong equation (*22*) represents a useful modification of van der Waals' equation, we propose to use this equation for liquid mixtures with certain alterations. The Redlich and Kwong equation of state is

$$P = \frac{RT}{v - b} - \frac{a}{T^{0.5}\, v(v + b)} \tag{13}$$

For any pure fluid, the two constants a and b can be related to the critical properties of that fluid by

$$a = \frac{\Omega_a R^2 T_c^{2.5}}{P_c} \tag{14}$$

$$b = \frac{\Omega_b R T_c}{P_c} \tag{15}$$

where Ω_a and Ω_b are dimensionless constants. If the con-

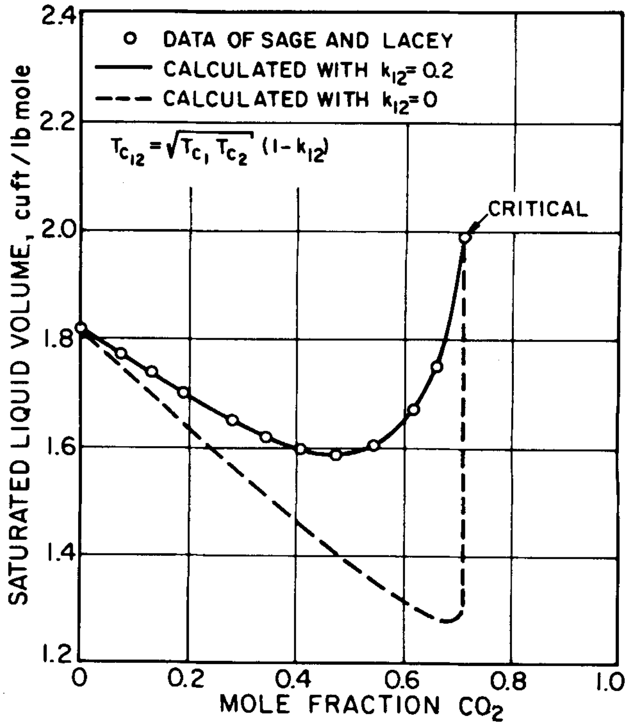

Fig. 3. Saturated liquid molar volume calculated with and without correction to geometric mean for Tc_{12} (*n*-butane–carbon dioxide at 160°F.).

Table 3. Acentric Factors and Dimensionless Constants in the Redlich and Kwong Equation of State for Saturated Liquids

	ω	Ω_a	Ω_b
Methane	0.013	0.4546	0.0872
Nitrogen	0.040	0.4540	0.0875
Ethylene	0.085	0.4290	0.0815
Hydrogen sulfide	0.100	0.4220	0.0823
Ethane	0.105	0.4347	0.0827
Propylene	0.139	0.4130	0.0803
Propane	0.152	0.4138	0.0802
iso-Butane	0.187	0.4100	0.0790
Acetylene	0.190	0.4230	0.0802
1-Butene	0.190	0.4000	0.0780
n-Butane	0.200	0.4184	0.0794
Cyclohexane	0.209	0.4060	0.0787
Benzene	0.211	0.4100	0.0787
iso-Pentane	0.215	0.3970	0.0758
Carbon dioxide	0.225	0.4184	0.0794
n-Pentane	0.252	0.3928	0.0767
n-Hexane	0.298	0.3910	0.0752
n-Heptane	0.349	0.3900	0.0740
n-Nonane	0.447	0.3910	0.0738

ditions at the critical point $\left[\left(\frac{\partial P}{\partial v}\right)_{T_c} = 0 \text{ and } \left(\frac{\partial^2 P}{\partial v^2}\right)_{T_c} = 0\right]$ are imposed, $\Omega_a = 0.4278$ and $\Omega_b = 0.0867$ for all fluids. Adoption of these values is equivalent to fitting the equation of state to experimental results in the critical region which, although the most sensitive, does not provide the best fit over a wide range of conditions. This is particularly true when the equation is applied to the liquid phase. If we accept universal values for Ω_a and Ω_b, we are, in effect, subscribing to a two-parameter theorem of corresponding states. However, Pitzer and others (*12* to *15*) have shown that the theorem of corresponding state requires a third parameter in order to be applicable to a wide class of substances. We propose, therefore, for each pure liquid, to fit the Redlich-Kwong equation to the P-V-T data of the saturated liquid and to evaluate the best Ω_a and Ω_b for each pure component. Fortunately, such data are readily available; results are given in Table 3 for nineteen common liquids. They differ slightly from the universal values, and show a trend with respect to acentric factor.

For application of Equation (13) to mixtures, we propose the following mixing rules:

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad [a_{ij} \neq (a_i a_j)^{1/2}] \tag{16}$$

$$b = \sum_i x_i b_i \tag{17}$$

where

$$a_{ii} = \frac{\Omega_{a_i} R^2 T_{c_i}^{2.5}}{P_{c_i}} \tag{18}$$

$$b_i = \frac{\Omega_{b_i} R T_{c_i}}{P_{c_i}} \tag{19}$$

$$a_{ij} = \frac{\frac{1}{4}(\Omega_{a_i} + \Omega_{a_j}) R T_{c_{ij}}^{1.5} (v_{c_i} + v_{c_j})}{0.291 - 0.04(\omega_i + \omega_j)} \tag{20}$$

PARTIAL MOLAR VOLUMES

The partial molar volume can be obtained from Equation (13) and the mixing rules, Equations (16) and (17), after performing the partial differentiation indicated in Equation (4):

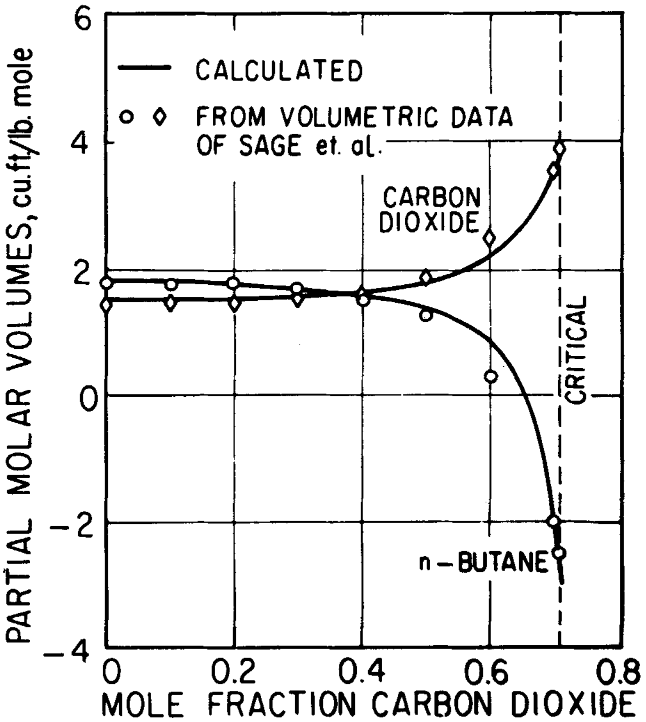

Fig. 4. Partial molar volumes in the saturated liquid phase of the *n*-butane–carbon dioxide system at 160°F.

$$\bar{v}_k = \frac{\frac{RT}{v-b}\left(1 + \frac{b_k}{v-b}\right) - \frac{2\left(\sum_i x_i a_{ki}\right) - a b_k/(v+b)}{v(v+b)T^{1/2}}}{\frac{RT}{(v-b)^2} - \frac{a}{T^{1/2}}\left[\frac{2v+b}{v^2(v+b)^2}\right]} \tag{21}$$

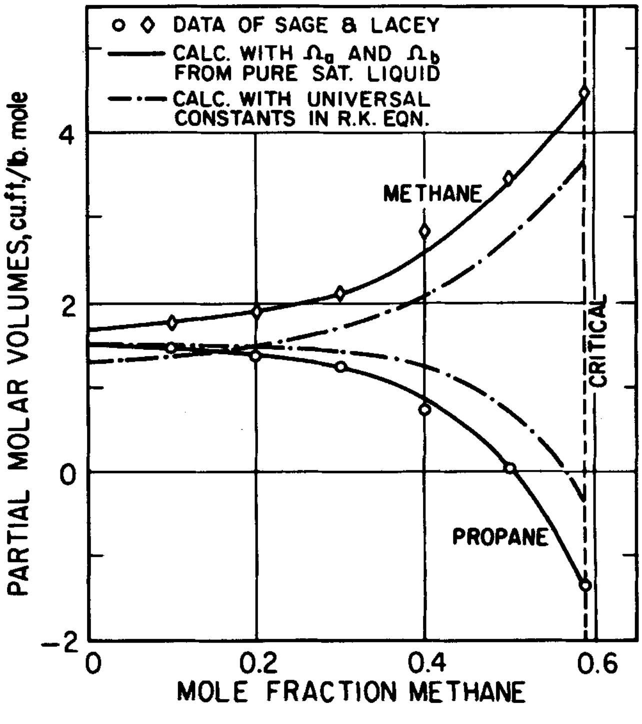

Fig. 5. Partial molar volumes in the saturated liquid phase of the propane-methane system at 100°F.

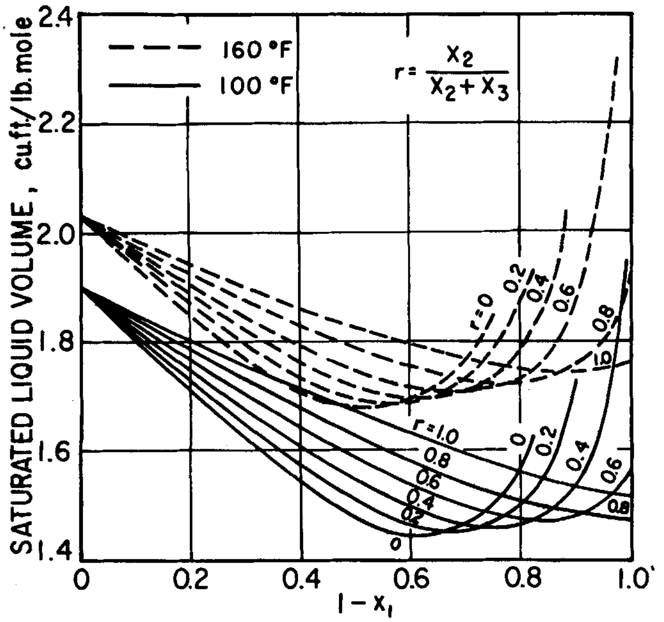

Fig. 6. Calculated saturated liquid molar volumes of the *n*-pentane (1)–propane (2)–methane (3) system.

Using v, the saturated liquid molar volume of the mixture, calculated previously, and Equations (16) through (20), one can readily calculate the partial molar volume of each component in a multicomponent liquid mixture from Equation (21). A computer program for performing the calculation is available (*2*).

Figures 4 and 5 show calculated partial molar volumes in the saturated liquid phase of the systems *n*-butane-carbon dioxide and propane–methane, including the critical region to be discussed later. The calculated values are compared with those computed from the volumetric data of Sage and Lacey (*25*). Agreement between calculated and experimental values is quantitative for both systems. The partial molar volumes of the lighter component (supercritical in these cases) and the heavier component show very different behavior in the critical region even for a system as simple as propane-methane. The partial molar volume of the lighter component approaches a large positive value, due to its dilative effect, and that of the heavier component approaches a large negative value, due to its condensing effect. As a result, pressure has exactly opposite effects on the activity coefficients of the lighter component and the heavier component, as indicated by Equation (2). The simple approximation of using partial molar volumes at infinite dilution leads to large error near the critical region.

Also shown in Figure 5 are the partial molar volumes calculated with the universal values $\Omega_a = 0.4278$ and $\Omega_b = 0.0867$. The results are much less satisfactory, indicating the need for evaluating Ω_a and Ω_b for each pure saturated liquid.

In a multicomponent system, the partial molar volume of each component depends on the liquid composition in a complex manner. Figures 6 and 7 show calculated saturated liquid volumes and partial molar volumes for the system *n*-pentane–propane–methane,* including the critical region.

CRITICAL REGION

In applying previously proposed pseudocritical rules to the critical region, it has often been found necessary to introduce an empirical exponent which depends on the proximity to critical conditions (*10*, *20*). In the following, we introduce a general proximity function which corrects the pseudocritical rules of Equations (7) and (8) in the critical region.

By definition, $T_R = 1.0$ and $v_R = 1.0$ at the critical point when the true critical constants of the mixture are used as the reducing parameters. Therefore, if the true criticals of a mixture can be calculated, the mixing rules, Equations (7) and (8), can be modified such that they will always converge to $T_R = 1.0$ and v_R 1.0 at the critical point. In the following, we use primes to indicate corrected pseudocriticals. Let

$$T'_{cM} = T_{cM} + (T_{cT} - T_{cM})\,\mathfrak{D}(T_R) \tag{22}$$

and

$$v'_{cM} = v_{cM} + (v_{cT} - v_{cM})\,\mathfrak{D}(T_R) \tag{23}$$

where T_{cT} and v_{cT} refer to the true critical temperature and true critical volume of the mixture, respectively. The second terms on the right-hand sides of Equations (22) and (23) correspond to the corrections added to the simple mixing rules, Equations (7) and (8). The function $\mathfrak{D}(T_R)$ represents the proximity of the system to its critical point; it must satisfy the two boundary conditions

$$\mathfrak{D}(T_R) \longrightarrow 0 \quad \text{for} \quad T_R < 0.93 \tag{24}$$

$$\mathfrak{D}(T_R) = 1 \quad \text{at} \quad T_R = 1.0 \tag{25}$$

The first boundary condition ensures that Equations (22) and (23) reduce to the simple mixing rules, Equations (7) and (8), for $T_R \leq 0.93$. The second boundary condition ensures that they converge to $T'_{cM} = T_{cT}$ and $v'_{cM} = v_{cT}$ at the critical point. We suggest the following empirical function which satisfies the above boundary conditions:

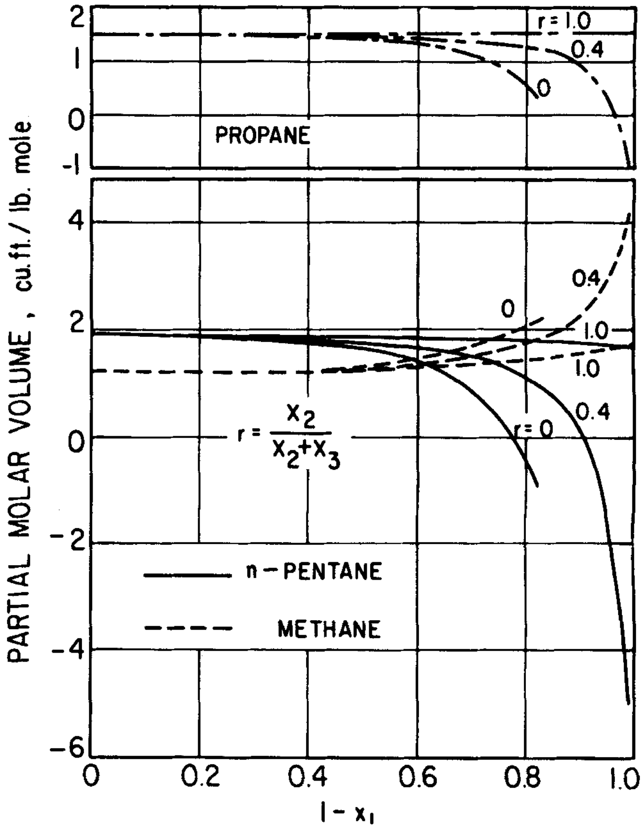

Fig. 7. Calculated partial molar volumes in the saturated liquid phase of the *n*-pentane (1)–propane (2)–methane (3) system at 100°F.

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*For pentane–propane, $k_{ij} = 0.01$, $\nu_{ij} = -1.018$ cu. ft./lb.-mole and $\tau_{ij} = 7.0$°R.

TABLE 4. COMPARISON OF CALCULATED AND EXPERIMENTAL SATURATED MOLAR LIQUID VOLUMES OF BINARY MIXTURES IN THE CRITICAL REGION

(Reduced temperature 0.93 to 1.00)

System* (1) (2)	ν_{12}, cu. ft./lb. mole	τ_{12}, °R.	T, °F.	Pressure range, lb./sq. in. abs.	x_2 (critical)	% Deviation Avg.	% Deviation Max.
n-Butane–carbon dioxide	−1.25	−46.4	100	800 to 1,057	0.954	2.3	4.3
			160	900 to 1,020	0.713	0.7	1.4
			220	600 to 942	0.498	0.7	3.0
Propane-methane	−0.875	89.7	40	1,200 to 1,474	0.7459	1.6	7.6
			100	950 to 1,353	0.5882	1.0	4.9
			160	384 to 1,020	0.3228	1.2	5.9
n-Butane-methane	−1.96	101.3	100	1,700 to 1,912	0.7236	1.6	4.5
			130	1,600 to 1,876	0.6718	1.6	3.4
			160	1,400 to 1,810	0.6165	2.2	2.8
			190	1,100 to 1,698	0.5503	3.4	5.1
			220	800 to 1,520	0.4722	4.6	9.5
			250	327.7 to 1,264	0.3602	3.3	10.3
n-Pentane-methane	−2.35	141.4	100	2,300 to 2,455	0.8236	2.5	5.2
			160	2,100 to 2,338	0.7665	2.6	3.7
			220	1,600 to 2,081	0.6705	3.1	4.7
			280	900 to 1,610	0.5211	2.3	3.2
			340	330 to 1,025	0.2950	0.9	2.1
Propylene-ethane	−0.273	−4.7	100	470 to 722	0.9300	0.8	2.5
			160	455 to 705	0.3500	2.8	10.5
Benzene-propane	−0.690	22.1	280	630 to 750	†	0.8	1.3
			340	710 to 850	†	1.4	1.6
			400	630 to 850	†	0.7	2.8
Hydrogen sulfide-methane	−0.958	29.3	40	1,770 to 1,949	0.5500	3.1	4.2
			100	1,500 to 1,907	0.3880	2.2	5.2
			160	779 to 1,660	0.2090	1.6	7.3

*k_{12} given in Table 1. Experimental data of binary systems are taken from Sage et al. (*24*, *25*).
†No critical composition reported.

$$\mathfrak{D}(T_R) = \exp\left[(T_R - 1)\left(2901.01 - 5738.92\, T_R + 2849.85\, T_R^2 + \frac{1.74127}{1.01 - T_R}\right)\right] \quad (26)$$

Equation (26) was found to be sufficiently general for all systems investigated. The reducing parameter for T_R in Equation (26) is the corrected pseudocritical temperature T'_{cM} rather than the true critical temperature which is adequate at the critical point only. As a result T'_{cM} appears on both sides of Equation (22) and iteration is required to solve for T'_{cM}. This is best done by rewriting Equation (22):

$$\left[\frac{(T/T_{cM})}{T_R} - 1\right] - \left[\frac{(T/T_{cM})}{(T/T_{cT})} - 1\right] \mathfrak{D}(T_R) = 0 \quad (27)$$

Equation (27) has only one unique solution for $T_R < 1.0$ which can be readily found by a numerical technique (for example, Reguli-falsi iteration with variable pivoting points). The method usually converges in a few iterations. From Equation (23), v_{cM} can then be obtained by direct substitution.

Equations (22) and (23) may be considered as more general pseudocritical rules applicable over the whole temperature range up to the critical point. With the corrected pseudocritical constants, the saturated molar volumes of liquid mixtures can be calculated from Equations (5) and (6) in the manner discussed before.

Figure 8 compares reduced temperatures and reduced volumes calculated for the system *n*-butane-carbon dioxide at 100°F., with the corrected pseudocriticals, Equations (22) and (23), and the uncorrected pseudocriticals, Equations (7) and (8). Whereas T_R and v_R based on corrected pseudocriticals converge to the right limit at the critical composition, those based on the uncorrected pseudocriticals at-

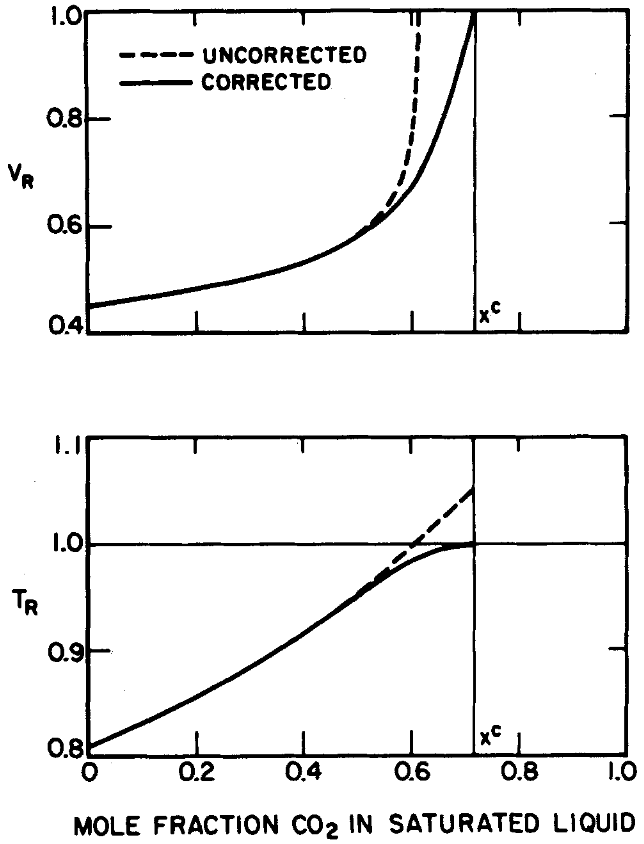

Fig. 8. Reduced temperature and reduced volume in the critical region with corrected and uncorrected pseudocritical constants (*n*-butane–carbon dioxide at 160°F.).

tain unreasonable values before reaching the critical composition. In the critical region, a small error in the reduced temperature produces a very large error in the calculated mixture volume as shown in Figure 8.

The true critical temperature and volume of mixtures, as needed in Equations (22) and (23), can be calculated from a correlation discussed in detail in reference *4*. The true critical constants are related to the composition by expressions using the surface fraction θ:

$$v_{cT} = \sum_i \theta_i v_{c_i} + \sum_i \sum_j \theta_i \theta_j \nu_{ij}, \quad (\nu_{ii} = 0) \tag{28}$$

$$T_{cT} = \sum_i \theta_i T_{c_i} + \sum_i \sum_j \theta_i \theta_j \tau_{ij}, \quad (\tau_{ii} = 0) \tag{29}$$

where

$$\theta_k = \frac{x_k \, v_{c_k}^{2/3}}{\sum_i x_i \, v_{c_i}^{2/3}} \tag{30}$$

The correlating parameters ν_{ij} and τ_{ij} are measures of the (small) deviations of the mixture criticals as given by a linear dependence on the θ fraction; they are characteristic of the *i-j* pair. Table 4 gives ν_{12} and τ_{12} for the seven systems investigated in this work. More extensive compilations of these parameters are given in the following paper (*4*).

Table 4 also summarizes calculations of saturated liquid volumes in the critical region for seven systems and twenty-five isotherms. In the critical region, deviations are larger than those found in the region where $T_R < 0.93$. Most of the largest deviations occur in the immediate vicinity of the critical point where experimental results are most likely to be in error. For example, Reamer et al. (*21*) reported that the accuracy of their liquid-phase mole fractions was about 0.013 mole fraction. If the critical mole fraction is known within ± 0.013, this uncertainty causes an error of about 5% in the critical volume.

In the critical region the calculations are strongly dependent on the accuracy of the calculated true critical temperature. An error of 0.5% in the calculated true critical temperature may cause an error of more than 5% in the calculated volume. The reduced volume is a very sensitive function of reduced temperature in the critical region; for a simple fluid ($\omega = 0$), the reduced volume at $T_R = 0.99$ is 0.7327, whereas at $T_R = 1.00$, $v_R = 1.0$ by definition. Thus, near the critical point, a 1% change in reduced temperature causes a change in reduced volume of about 30%. This extreme sensitivity of volumetric properties to small changes in temperature or composition is an inherent nature of the critical state and cannot easily be eliminated, neither by experiment nor by calculation.

Once the saturated liquid volume is known, partial molar volumes can be calculated from Equation (21) in exactly the same manner as that discussed before. Calculated partial molar volumes in the critical region are shown in Figures 4, 5, and 7 for the binary systems *n*-butane–carbon dioxide and propane–methane, and for the ternary system *n*-pentane–propane–methane.

CONCLUSION

This work presents a method for predicting partial molar volumes in a multicomponent liquid mixture at saturation. Calculated partial molar volumes depend strongly on the liquid composition, especially in the critical region where the partial molar volume of the heavier component may change sign. Calculated results are in quantitative agreement with the limited experimental data now available.

The calculations are sensitive to the characteristic energy between two dissimilar molecules which, in general, is lower than that given by the geometric mean. These characteristic energies have been determined for a number of systems from several binary data sources, such as second virial cross coefficients and binary saturated liquid volumes. For a given binary system, characteristic energies found from different sources generally agree well with each other.

With partial molar volumes, the effect of pressure on liquid-phase activity coefficients can be taken into account. By separating the effect of pressure from that of composition, one can subject experimental liquid phase activity coefficients to rigorous thermodynamic analysis. Such analysis permits meaningful interpretation and correlation of binary, high-pressure, vapor-liquid equilibrium data and facilitates prediction of multicomponent phase behavior.

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NOTATION

a, b = constants in Redlich and Kwong equation of state
k_{ij} = characteristic constant for *i-j* interaction
n_k = number of moles of component *k* in the mixture
P = total pressure
P_c = critical pressure
R = gas constant
T = temperature
T_c = critical temperature
T_{cM} = pseudocritical temperature of a mixture
T'_{cM} = corrected pseudocritical temperature of a mixture
T_{cT} = true critical temperature of a mixture
T_R = reduced temperature
V = total volume of a liquid mixture
v = molar volume of liquid or liquid mixture
$\bar{v}_k$ = partial molar volume of component *k* in the liquid phase
v_{cM} = pseudocritical volume of a mixture
v'_{cM} = corrected pseudocritical volume of a mixture
v_{cT} = true critical volume of a mixture
v_R = reduced volume
$v_R^{(j)}$ = generalized reduced molar-volume function of saturated liquid, as defined by Equation (6)
x = mole fraction in liquid phase
$\gamma_k^{(P)}$ = activity coefficient of component *k* at pressure *P*
$\gamma_k^{(P^r)}$ = activity coefficient of component *k* at some constant reference pressure
θ = surface fraction as defined by Equation (30)
ν_{ij} = correlating parameter for true critical volume of *i-j* binary
τ_{ij} = correlating parameter for true critical temperature of *i-j* binary
Φ = volume fraction as defined by Equation (10)
Ω_a, Ω_b = dimensionless constants in Redlich and Kwong parameters as defined by Equations (14) and (15)
ω = acentric factor

Subscripts

c = critical
i, ii = component i
j, jj = component j
ij = *i-j* pair
M = mixture
R = reduced quantity

Superscript

0 = standard state

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Vapor-Liquid Equilibria at High Pressures: Calculation of Critical Temperatures, Volumes, and Pressures of Nonpolar Mixtures

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An analysis of critical data for a large number of binary mixtures of normal fluids shows that the critical temperature and the critical volume can each be expressed as quadratic functions of the surface fraction. Each of these functions requires one adjustable parameter characteristic of the binary pair; for any family of chemical components, these parameters, upon suitable reduction, follow definite trends. It was shown that the surface fraction gives much better correlation than any other size-weighted variable. For the critical pressure, however, no quadratic function was adequate. To calculate critical pressures, the correlations for critical temperature and critical volume were used in conjunction with a slightly altered version of the Redlich-Kwong equation.

Generalizations to systems containing more than two components follow without additional assumptions. The methods presented in this paper provide good estimates for critical constants of multicomponent mixtures. These are particularly useful for analyzing and correlating vapor-liquid equilibria in the critical region.

The critical properties of pure fluids have received much attention and as a result of much experimental work, dating back nearly 100 years (*3*, *6*), as well as semiempirical correlations (*56*), it is now possible to make good estimates of the critical temperature, pressure, and volume of most pure fluids encountered in typical chemical engineering work. The critical properties of mixtures, however, are not known nearly as well, although experimental data are available for a surprisingly large number of binary mixtures (*58*).

Critical properties of mixtures are required in petroleum and natural gas engineering and for rational design of separation equipment and chemical reactors at high pressures.